

**DEVELOPMENT OF ASYMMETRIC POLYETHERSULFONE (PES)
MEMBRANE FOR O₂/N₂ SEPARATION BY USING DIFFERENCE TECHNIQUE
OF MEMBRANE FORMATION**

MARDHIANA BINTI ISMAIL

**Thesis submitted in fulfillment of the requirements
for the award of the Degree of
Bachelor of Chemical Engineering (Gas Technology)**

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

DECEMBER 2010

ABSTRACT

Asymmetric polyethersulfone membrane for gas separation by varying the step of membrane formation have been successfully developed. The casting solution contained of polyethersulfone (PES) as polymer, 1-methyl-2-pyrrolidone (NMP) was employed as a solvent while distilled water (H_2O) was used as nonsolvent additives (NSA). Firstly, the casting solution with the concentration of 32.62 wt% PES, 60.58 wt% NMP and 6.8 wt% H_2O were used to produce polyethersulfone flat sheet asymmetric membrane. Then, the casting solution was cast on the glass plate by using a casting block with constant thickness which is 400 μm at room temperature ($\approx 25^\circ C$ and average relative humidity is 65%) with difference way of phase inversion which are dry/wet phase inversion, dry at room temperature and dry in oven at $40^\circ C$. The produced membranes were characterized by pure gas permeation experiments by using permeation test unit and the morphology of the membrane was identified using Scanning Electron Microscopy (SEM). For permeation test, oxygen (O_2) and nitrogen (N_2) were used as a test gases for both uncoated and coated membranes. For the coated membrane, pressure-normalized flux and selectivity showed a more constant trend with increasing feed pressure compare to uncoated membrane for all method of drying process. Coated membrane exhibited higher selectivity than uncoated membranes due to coating of the skin layer defects. Consequently, the best selectivity was found using the dry/wet phase inversion compared than others. The pressure-normalized flux and O_2/N_2 selectivity were found 25.39 GPU for O_2 and 10.12 GPU for N_2 and 2.53 respectively. For the Scanning Electron Microscopy (SEM) result, flat sheet membrane prepared by dry/wet phase inversion show the formation of asymmetric membrane with a thin and dense skin layer supported by a thick porous sublayer compared to other which dry at room temperature and dry in oven at $40^\circ C$ with formation of symmetric membrane with the diameter of the pores is almost constant throughout the cross section of the membrane. flat sheet membrane prepared by dry/wet phase inversion show the a dense skin layer and sublayer with existing of microvoid and macrovoid while flat sheet membrane prepared by dry at room temperature and dry in oven at $40^\circ C$ show the formation of porous layer with small microvoid which look sponge like and existing of porous layer with macrovoid respectively. As a conclusion, dry/wet phase inversion technique has successfully developed asymmetric membranes and can be applied for O_2/N_2 separation.

ABSTRAK

Membran asimetrik polietersulfona untuk pemisahan gas dengan memvariasikan langkah pembentukan membran telah berjaya dihasilkan. Larutan tuangan yang mengandungi polietersulfona (PES) sebagai polimer, 1-metil-2-pirolidon (NMP) bertindak sebagai pelarut manakala air suling (H_2O) digunakan sebagai bahan tambah bukan larut (NSA). Pertama, larutan tuangan dengan kepekatan 32.wt62% PES, 60.58wt% NMP dan 6.8wt% H_2O digunakan untuk menghasilkan kepingan rata membrane asimetrik polietersulfona. Kemudian, larutan tuangan dituang pada kepingan kaca dengan menggunakan blok tuangan dengan ketebalan yang sama 400 μ m dan pada suhu bilik ($\approx 25^\circ C$ dan purata kelembapan relatif 65%) dengan perbezaan cara balikan iaitu fasa balikan kering/basah, kering pada suhu bilik dan kering dalam oven pada $40^\circ C$. Membrane yang dihasilkan dicirikan dengan ujian penelapan gas tulen menggunakan unit ujian penelapan dan morfologi membrane dikenalpasti menggunakan Mikroskop Elektron Imbasan (SEM). Bagi ujian penelapan, Oksigen (O_2) dan Nitrogen (N_2) telah digunakan sebagai gas ujian untuk kedua-dua membrane bersalut dan membrane tidak bersalut. Untuk membran bersalut, fluks tekanan-ternormal dan kememilhan menunjukkan trend yang lebih konsten dengan peningkatan tekanan suapan berbanding dengan membran yang tidak bersalut untuk kesemua kaedah proses pengeringan. Membran yang bersalut menunjukkan kememilhan yang lebih tinggi daripada membrane yang tidak bersalut disebabkan lapisan permukaan membran yang cacat. Akibatnya, kememilhan yang terbaik telah ditemui menggunakan fasa balikan kering/basah berbanding daripada yang lain. Fluks tekanan-ternormal dan kememilhan O_2/N_2 mendapati 25.39 GPU untuk gas Oksigen (O_2), 10.12 GPU untuk gas Nitrogen (N_2) dan 2.53 masing-masing. Untuk hasil Mikroskop Elektron Imbasan (SEM), kepingan rata membrane yang disediakan menggunakan teknik fasa balikan kering/basah menunjukkan pembentukan membrane asimetrik dengan satu lapisan kulit yang tipis dan padat yang disokong dengan lapisan bawah yang tebal berbanding dengan yang lain iaitu kering pada suhu bilik dan kering dalam oven pada $40^\circ C$ dengan pembentukan membrane simetrik dengan diameter pori-pori yang hamper sama sepanjang keratin rentas membran. Kepingan rata membran yang disediakan menggunakan fasa balikan kering/basah menunjukkan satu lapisan padat dan lapisan bawah dengan kehadiran microvoid dan macrovoid manakal kepingan rata membran yang disediakan menggunakan kering pada suhu bilik dan kering dalam oven pada $40^\circ C$ menunjukkan pembentukan lapisan berpori dengan microvoid kecil yang kelihatan seperti span dan kehadiran lapisan berpori dengan macrovoid masing-masing. Sebagai kesimpulan, teknik fasa balikan kering/basah telah berjaya menghasilkan membran asimetrik polyethersulfona dan boleh dilaksanakan untuk pemisahan O_2/N_2 .

TABLE OF CONTENT

| | Page |
|--|-------------|
| SUPERVISOR’S DECLARATION | iii |
| STUDENT’S DECLARATION | iv |
| ACKNOWLEDGEMENT | vi |
| ABSTRACT | vii |
| ABSTRAK | viii |
| TABLE OF CONTENTS | ix |
| LIST OF TABLES | xii |
| LIST OF FIGURES | xiii |
| LIST OF SYMBOLS | xvi |
| CHAPTER 1 INTRODUCTION | |
| 1.1 Research Background | 1 |
| 1.2 Problem Statement | 3 |
| 1.3 Objectives of Study | 3 |
| 1.4 Scopes of Research | 4 |
| 1.5 Rationale and Significant | 4 |
| CHAPETER 2 LITERARURE REVIEW | |
| 2.1 Membrane Technology | 5 |
| 2.2 History Development of Membranes | 9 |
| 2.3 Membranes Classification | 10 |
| 2.4 Gas Separation by using Membranes | 11 |
| 2.5 Characteristics of Membrane For Gas Separation | 13 |
| 2.6 Fundamental of Gas Permeation | 14 |
| 2.7 Asymmetric Membrane Formation | 18 |
| 2.7.1 Characteristic of Asymmetric Membranes | 20 |
| 2.8 Different technique on Membrane Formation | 21 |

| | | |
|---------|---|----|
| 2.8.1 | Thermal Induced Phase Separation Technique | 22 |
| 2.8.2 | Air casting Dope Solution Technique | 23 |
| 2.8.3 | Precipitation From the Vapour Phase Technique | 23 |
| 2.8.4 | Immersion Precipitation Technique | 23 |
| 2.8.4.1 | Dry Phase Inversion | 25 |
| 2.8.4.2 | Wet Phase Inversion | 26 |
| 2.8.4.3 | Dry/Wet Phase Inversion | 27 |

CHAPTER 3 METHODOLOGY

| | | |
|-------|---|----|
| 3.1 | Materials | 29 |
| 3.1.1 | Polyethersulfone (PES) | 29 |
| 3.1.2 | 1-Methyl-2-Pyrrolidone @ NMP | 30 |
| 3.1.3 | Physical Properties of Nonsolvent Additives and Coagulation Bath | 31 |
| 3.1.4 | Physical Properties of Gases | 32 |
| 3.2 | Research Design | 33 |
| 3.3 | Preparation of Casting Solution (Dope) | 34 |
| 3.4 | Membrane Casting | 35 |
| 3.5 | Membrane Coating | 38 |
| 3.6 | Gas Permeation Test | 39 |
| 3.7 | Scanning Electron Microscopy (SEM) | 41 |

CHAPTER 4 RESULT AND DISCUSSION

| | | |
|-------|---|----|
| 4.1 | Effect of Drying Technique on O ₂ /N ₂ Separation Performance | 42 |
| 4.1.1 | Performance of Uncoated Polyethersulfone Membranes | 42 |
| 4.1.2 | Performance of Coated Polyethersulfone Membranes | 45 |
| 4.2 | Effect of Pressure on Gas Separation Membrane Performance | 48 |
| 4.2.1 | Performance of Uncoated Polyethersulfone Membranes | 48 |
| 4.2.2 | Performance of Coated Polyethersulfone Membranes | 50 |

| | | |
|-------|---|----|
| 4.3 | Effect of Drying Technique on Morphology of Uncoated and Coated Membrane | 54 |
| 4.3.1 | Cross Section and surface layer of uncoated/coated membrane image at different types of drying techniques | 54 |

CHAPTER 5 CONCLUSION AND RECOMMENDATION

| | | |
|-------------------|----------------|----|
| 5.1. | Conclusion | 63 |
| 5.2. | Recommendation | 65 |
| REFERENCES | | 67 |
| APPENDICES | | 71 |

LIST OF TABLES

| Table No. | Title | Page |
|------------------|---|-------------|
| 2.1 | Membrane separation, membrane type, driving force and its applications | 7 |
| 2.2 | Historical of membrane separation technology | 9 |
| 2.3 | Type, structure and preparation of synthetic membranes | 10 |
| 2.4 | Gas membrane application | 12 |
| 2.5 | Materials for gas separating membranes | 12 |
| 2.6 | Calculated separation factors based on Knudsen flow for the selected binary gas mixture | 18 |
| 3.1 | Physical, mechanical strength and thermal properties of polyethersulfone (PES) | 30 |
| 3.2 | Physical and chemical properties of NMP | 31 |
| 3.3 | Physical properties of nonsolvent additives and coagulation bath | 32 |
| 3.4 | Properties of pure oxygen (O ₂) and nitrogen (N ₂) | 32 |
| 4.1 | Separation properties of uncoated membranes at different drying technique | 43 |
| 4.2 | Separation properties of coated membranes at different drying technique | 46 |

LIST OF FIGURES

| Figure No. | Title | Page |
|-------------------|--|-------------|
| 2.1 | Typical membrane process for gas separation | 14 |
| 2.2 | Schematic presentation of mechanism for permeation of gases through membranes | 15 |
| 2.3 | Cross section view of asymmetric membrane | 19 |
| 2.4 | Phase inversion techniques | 22 |
| 2.5 | Coagulation path of a polymer film with initial composition A when brought in contact with a nonsolvent vapor phase saturated with solvent | 23 |
| 2.6 | Shematic phase diagram for ternary consisting of polymer /solvent/nonsolvent. | 24 |
| 2.7 | Schematic of dry phase inversion process | 26 |
| 2.8 | Schematic of wet phase inversion process | 26 |
| 2.9 | Schematic dry/wet phase inversion process | 27 |
| 3.1 | Molecular structure of polyethersulfone | 30 |
| 3.2 | Formula structure of N-methyl-2-pyrrolidone (NMP) | 31 |
| 3.3 | The experiment workflow of research study | 33 |
| 3.4 | Casting solution preparation system | 34 |
| 3.5 | Schematic Preparation of flat sheet membrane by immersion precipitation | 35 |
| 3.6 | Step involve in the dry/wet phase inversion | 36 |
| 3.7 | Step involve in the dry phase inversion (room temperature) | 37 |
| 3.8 | Step involve in the dry phase inversion (dry in oven) | 38 |
| 3.9 | Gas Permeation test apparatus | 39 |

| | | |
|------|---|----|
| 3.10 | Schematic Diagram of Permeation cell | 40 |
| 4.1 | Pressure-normalized flux and selectivity vs drying technique of uncoated membrane at different drying technique at 3 bar | 45 |
| 4.2 | Pressure-normalized flux and selectivity vs drying technique of coated membrane at different drying technique at 3 bar | 47 |
| 4.3 | Pressure-normalized flux and selectivity vs pressure of uncoated membrane using dry/wet phase inversion at different pressure | 49 |
| 4.4 | Pressure-normalized flux and selectivity vs pressure of uncoated membrane using dry phase inversion (dry-casting at room temperature) at different pressure | 49 |
| 4.5 | Pressure-normalized flux and selectivity of uncoated membrane using dry 5phase inversion (dry in oven at 40°C) at different pressure | 50 |
| 4.6 | Pressure-normalized flux and selectivity vs pressure of coated membrane using dry/wet phase inversion at different pressure | 51 |
| 4.7 | Pressure-normalized flux and selectivity of coated membrane using dry phase inversion (dry at room temperature) at different pressure | 52 |
| 4.8 | Pressure-normalized flux and selectivity vs pressure of coated Membrane using dry phase inversion (dry in oven at 40°C) at different pressure | 53 |
| 4.9 | Cross section of uncoated membrane image by using dry/wet phase inversion technique (i) 1500X magnification (ii) 400X magnification | 54 |
| 4.10 | Cross section of coated membrane image by using dry/wet phase inversion technique (i) 1500X magnification (ii) 400X magnification | 55 |
| 4.11 | Cross section of uncoated membrane image by using dry phase inversion (dry at room temperature) technique (i) 1500X magnification (ii) 400X magnification | 57 |
| 4.12 | Cross section of coated membrane image by using dry phase inversion (dry at room temperature) technique | 59 |

| | | |
|------|---|----|
| | (i) 1500X magnification (ii) 400X magnification | |
| 4.13 | Cross section of uncoated membrane image by using dry phase inversion (dry in oven at 40°C) technique (i) 1500X magnification (ii) 400X magnification | 59 |
| 4.14 | Cross section of coated membrane image by using dry phase inversion (dry in oven at 40°C) technique (i) 1500X magnification (ii) 400X magnification | 60 |
| 4.15 | Surface layer of uncoated membrane image at different drying technique at 30X magnification (i) Dry/wet phase inversion,(ii) Dry phase inversion (dry at room temperature (ii) dry phase inversion (dry in oven at 40°C) | 62 |
| 4.16 | Surface layer of uncoated membrane image at different drying technique at 30X magnification (i) Dry/wet phase inversion,(ii) Dry phase inversion (dry at room temperature (iii) dry phase inversion (dry in oven at 40°C) | 63 |

LIST OF SYMBOLS

| | |
|------------------|----------------------------------|
| PDMS | Polydimethylsiloxane |
| O ₂ | Oxygen |
| N ₂ | Nitrogen |
| CO | Carbon Monoxide |
| CH ₄ | Methane |
| H ₂ O | Water |
| SEM | Scanning Electron Microscopy |
| H ₂ | Hydrogen |
| H ₂ S | Hydrogen Sulphide |
| NMP | 1-Methyl-2-Pyrrolidone |
| PDMS | Polydimethylsiloxane |
| AFM | Atomic Force Microscopy |
| NSA | Nonsolvent Additive |
| PES | Polyethersulfone |
| TPIS | Thermal Induced Phase Separation |
| GPU | Gas Permeation Unit |
| RT | Room Temperature |

Parameters/ Symbol

| | |
|--------------|------------------------|
| P | Pressure |
| R | Gas Constant |
| T | Absolute temperature |
| M | Molecular Weight |
| V | Molar Volume |
| \AA | Angstrom |
| T_g | Transition Temperature |
| r | Radius |
| λ | Mean free path |

| | |
|--------|------------------------|
| η | Viscosity |
| R | Universal Gas Constant |
| T | Temperature |
| M | Molecular weight |

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Membrane separation process has become one of the emerging technologies, which have undergone a rapid growth during the past few decades. According to Paul and Yompol'skii (1994), membrane is a phase or a group of phase that lies between two different phases, which is physically and/ or chemically distinctive from both of them and which, due to its properties and the force field applied, is able to control the mass transport between these phases. In simple word, membranes are thin layers, that can have significantly different structures, but all have the common feature of selective transport to different components in feed.

Gas separations become a major industrial application of membrane technology only during the past 15 years, but the study of gas separation actually began long before that period (Baker, 2000). According to Ismail *et al.* (2003), phase inversion techniques can be categorized into four different techniques which thermal precipitation, air casting of dope solution, precipitation from the vapour phase and immersion precipitation. Phase inversion is important stage in the membrane formation to get high performance which high selectivity and permeability of membrane and defect-free asymmetric polyethersulfone (PES) membrane for gas separation application. According to previous researchers, Ismail and Lai identified that correlation of primary dry/wet phase inversion with rheological aspects had successfully developed defect-free and ultrathin-skinned asymmetric membrane for gas separation. For the result, membrane by polymer solution containing solvent ratio

which 4.0 wt % wt% resulted in asymmetric membrane having a thin and porous skin layer with a macrovoid-filled open cell substructure were formed.

From different perspective, Matsuyama *et al.* (1997) and Altinkaya and Ozbas (2003) had expressed that ultrathin-skinned and defect-free asymmetric membrane by dry-casting method. As a result, only solvent whereas acetone evaporated because used the high boiling point of nonsolvent in membrane formation. (Matsuyama *et al.*, 1997). Membrane formation of dry-casting method have correlation with concentration with water (nonsolvent) in the initial casting solution and evaporation conditions. Without altering polymer, solvent, or nonsolvent, it is possible to vary the structure from dense to porous asymmetric by either increasing the nonsolvent composition or decreasing the air velocity during evaporation as has been carried out by Altinkaya and Ozbas (2003). As results, porous asymmetric membrane produced with acetone 80m³ %, water 10m³ % and cellulose acetone 10m³ %.

Integral skinned asymmetric gas separation membranes were prepared by (i) dry, (ii) wet, and (iii) dry/wet phase inversion processes. (Ismail *et al.*, 2003). As a results, membrane made by dry/wet phase inversion showed optimum gas separation performance. The average O₂/N₂ and He/N₂ selectivity of these membranes were within 85% of those determined for a dense (Pinnau and Koros, 1991). The average apparent skin layer thickness of all samples tested was 270 Å. For scanning electron microscopy, it consists of an ultrathin skin layer, a tightly packed nodular transition layer, and an open cell, sponge-like substructure. Dry phase inversion membranes exhibited extremely low gas fluxes due to thick (17.5µm) skin layers. On the other hand, wet phase inversion membranes showed O₂/N₂ selectivity < 1, indicating that gas transport was determined by pore flow through skin layer defects (Pinnau and Koros, 1991).

Thus, different technique of membrane formation will be studied where it strongly believes that will affect the permeability and the selectivity of the membrane.

1.2 PROBLEM STATMENT

The different technique of membrane formation is one of important role to fabricate asymmetric polyethersulfone membrane for gas separation application. Pinnau and Koros (1992) reported that among the dry, wet and dry/wet phase inversion that investigated, it showed dry/wet phase inversion showed optimum gas separation performance. Even though dry/wet was proved as the best immersion precipitation in membrane formation, none of the researcher studied on dry-casting phase inversion by using oven as medium to drying process. Membrane preparation one of the factor that influence the performance of the membrane which increasing the pressure-normalized flux (Peinemann, 1996). High pressure - normalized flux does not exhibit that the membrane is in a good performance. Therefore, high selectivity is needed to develop membrane with defect free. Therefore, this study focus on the different step of membrane formation which is (i) dry-casting at room temperature (ii) dry-casting in oven at 40°C (iii) dry/wet phase inversion in development and optimization of the membrane formation process of asymmetric polyethersulfone membrane for gas separation.

1.3 OBJECTIVES OF THE STUDY

Based on the problem statement described in the previous section, the objectives of the research are:

1. To develop a flat sheet polyethersulfone (PES) membrane for O₂/N₂ separation application
2. To study the effect of different technique of membrane formation on the morphology of the produced membrane.

1.4 SCOPES OF RESEARCH

In order to achieve the objective as stated above, the following scopes of work are identified:

1. Developing new types of membrane by applying differences step of membrane formation to fabricate high performance and defect-free asymmetric polyethersulfone (PES) membrane for gas separation application
2. Characterization of the developed membrane using pure gases N_2 and O_2 as test gases.
3. Differentiate the performance of developed membrane for uncoated and coated membrane.
4. Morphological studies of the surface layer and cross section of the developed membrane using Scanning Electron Microscopy (SEM).

1.5 RATIONALE AND SIGNIFICANT

As know, nowadays, membrane have gained important place in separation technology and are used in broad range of application. Rationale and significant of thus study are membrane process can be operated at low energy consumption compared to the conventional gas separation methods such as low temperature distillation and it will produced high and quality product (Peinemann and Pinnau, 1988). Besides that membrane separation processes offered more capital and energy efficiency compared to conventional separation processes in some application (Chung *et al.*, 1997; Bickel and Koros, 1999). The membrane process requires simple, easy to operate and compact equipment. The process has acquired a significant industrial role in industrial scenario in term of economical considerations, as gases occupy a central position in the chemical feed stock industry (Pandey and Chauhan, 2001).

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE TECHNOLOGY

In recent years, membrane-based technology has found use in industrial processes (Koros, 2004). It is widely applied in purification, concentration and fractionation of fluid mixtures with evident advantages of energy saving, compactness, ease of operation and maintenance, continuous operation, and environmental friendliness. Membranes have found applications in areas that were previously dominated by more traditional processes, such as distillation, absorption, adsorption, and extraction and filtration. Even if in many cases membranes could not completely replace these technologies, hybrid systems combining membranes with one of the traditional techniques are accepted as attractive options (Spillman, 1989). According to Matsuura *et al.* (1996), the membrane can be a liquid, or a gel, and the bulk phases can be liquid, gas, or vapor.

Membranes can be classified according to their structures. Homogeneous or asymmetric membranes each have a structure that is the same across the thickness of the membrane. These membranes can be porous or have a rather dense uniform structure. Heterogeneous or asymmetric membrane can be categorized into three basic structures:

- a) Integrally skinned asymmetric membrane with a porous skin layer
- b) Integrally skinned asymmetric membrane with a dense skin layer
- c) Thin film composite membranes

Porous membranes are mostly fabricated by a process called phase inversion and are applied in dialysis, ultrafiltration, and microfiltration, whereas integrally skinned asymmetric membrane with a dense skin layer are applied in reverse osmosis and gas separation applications (Pereira *et al.*(2000). Naylor (1996) has stated that membrane processes may be considered to approach ideal separation processes, in that they offer the possibility of selectively permeating one component from a mixture whilst rejecting others, in a continuous steady state.

The market are rather diverse where most in medicine and chemical industry and the most significant industry market segments are medical devices and water treatment. For example, the worldwide sales of synthetic membranes are estimated at over US \$2 billion in 2003 (Srikanth, 2003). Membrane processes involve very different processes and hence it might be expected that a number of very different membranes is necessary. The most important membrane qualities to be considered are (Rautenbach and Albrecht, 1989):

- a) High selectivity
- b) High permeability
- c) Mechanical strength
- d) Temperature stability
- e) Chemical resistance

Membrane processes can classify by the transportation of selected species passing through it by driving forces across the membrane (Sirkar and Winston Ho, 1992). Membrane separation can be illustrates in the Table 2.1

Table 2.1: Membrane separation, membrane type, driving force and its applications (Scott, 1998 and Matsuura *et al.*,2008)

| Membrane separation | Membrane type | Driving force | Applications |
|------------------------------------|---|---|---|
| Microfiltration | Symmetric and asymmetric microporous | Hydrostatics pressure | 1) Clarification and biological stabilization in the beverage industry 2) Purification of fluids in semiconductor manufacturing industry 3) Sterilization (in the food and pharmaceutical industry) |
| Ultrafiltration | Asymmetric microporous | Hydrostatics pressure | Separation of macromolecular solutions: 1) Electrodialysis pretreatment 2) Juice clarification 3) Dewaxing 4) Water treatment 5) Cheese whey treatment 6) Separation of oil/ water emulsion 7) Egg-white preconcentration 8) Recovery of textile sizing agents 9) Electrophoretic paint |
| Nanofiltration | Asymmetric | Hydrostatics pressure | Separation of small organic compounds and selected salts from solutions: 1) Water treatment 2) Product and chemical paint 3) Concentration/ dewatering 4) Fractionation of monosolvent and divalent cations 5) Water softening |
| Reverse osmosis or hyperfiltration | Asymmetric, composite with homogeneous skin | Asymmetric, composite with homogeneous skin | Separation of microsolute and salts from solutions: 1) Sea water and brackish water desalination 2) Waste water treatment (industrial and municipal, pulp and paper, textiles waste water) 3) Petroleum industry 4) Recovery of plating chemical from wastewaters and process waters in the electroplating and metal-finishing industry 5) Production of boiler quality water for steam generation |

Table 2.1: (Continued)

| Membrane separation | Membrane type | Driving force | Applications |
|----------------------------|--|--|--|
| Gas permeation | Asymmetric or composite, homogeneous or porous polymer | Hydrostatic pressure, concentration gradient | Separation of gas mixture: 1) Hydrogen recovery <ul style="list-style-type: none"> • Synthesis gas ration adjustment (H_2/CO) • H_2 recovery from hydroprocessing purge streams • H_2 recovery from ammonia plant purge streams and other petrochemical plants stream 2) Oxygen/nitrogen separation 3) Helium recovery 4) Biogas processing |
| Dialysis | Dialysis | Concentration gradient | Separation of micro-solutes and salts from macromolecular solutions 1) Hemofiltration and hemodiafiltration 2) Alcohol reduction of beverages |
| Pervaporation | Asymmetric, composite nonporous | Concentration gradient, vapor pressure | Separation of mixtures of volatile liquids 1) Removal of organic apors from air 2) Water removal from liquid organics 3) Organic/ organic separation |
| Vapour permeation | Composite nonporous | Concentration gradient | Separation of volatile vapors from gases and vapors |
| Membrane distillation | Microporous | Temperature | Separation of water from non volatile solutes |
| Electrodialysis | Ion exchange, homogeneous or microporous polymer | Electrical potential | Separation of ions from water and non-ionic solutes 1) Desalination of brackish water 2) Production of table salts 3) Concentration of RO brines |
| Electrofiltration | Microporous, charged membrane | Electrical potential | De-watering of solutions of suspended solids |
| Liquid membranes | Microporous, liquid reaction | Concentration, reaction | Separation of ions and solutes from aqueous solutions |

2.2 HISTORY DEVELOPMENT OF MEMBRANES

Systematic studies of membrane phenomena can be traced to the 18th century philosopher scientists. Table 2.2 below show historical developments in membrane technology.

Table 2.2: Historical of membrane separation technology (Baker, 2000 and Naylor, 1996)

| Year | Philosopher | Inventor |
|---------------|---|--|
| 1748 | Abbé Nolet | -Coined the word osmosis to describe permeation of water through a diaphragm |
| 1866 | Thomas Graham | -Postulated that the permeation process involves a solution-diffusion process by which penetrant first dissolved in the membrane and then diffused through by the same process as that occurring in liquids. -He demonstrates that atmospheric air could be enriched from 21% to 41% oxygen using a natural rubber membrane. -He showed that the permeation rate of the gas molecules was reduced as the film thickness increased. |
| 1887 | van't Hoff | -Develop his limit law, which explains the behavior of ideal dilute solution, this work led directly to the von't Hoff equation. |
| | Maxwell et. al | -The concept of a perfectly selective semipermeable membrane in developing the kinetic theory of gases. |
| 1907 | Bechhold | -Devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test. |
| 1930 | Elford, Zsigmondy and Bachmann and Ferry | -Improved on Bechhold's technique -Microporous collodion membranes were commercially available. |
| Next 20 years | -This early microfiltration membranes technology was expanded to other polymers, notably cellulose acetate. Membrane found their first significant application in the testing of drinking water at the end of World War II. -Drinking water supplies serving large communities in Germany and elsewhere in Europe has broken down and filters to test for water safety were needed urgently. | |

Table 2.2: (Continued)

| | |
|------|--|
| | -The research effort to develop these filters, sponsored by the US Army, was later exploited by the Milipore Corporation |
| 1980 | <ul style="list-style-type: none"> -Microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established process with large plants installed worldwide. -The principle was the emergences of industrial membrane gas separation processes. -The first major development was the Monsanto Prism® membrane for hydrogen separation -Dow was producing systems to separate carbon dioxide from natural gas -Gas separation technology is evolving and expanding rapidly, further substantial growth will be seen in the coming years. -Final development was introduced by GFT, a small German engineering company, of the first commercial pervaporation of alcohol. More than 100 ethanol and isopropanol pervaporation dehydration plants have now been installed. |

2.3 MEMBRANE CLASSIFICATION

The membrane is clearly the most important part of the separation process. The properties of membrane are controlled by its material and structure (Matsuura *et al.*, 2008). Table 2.3 below summarizes the types and properties of some synthetic membranes.

Table 2.3: Type, structure and preparation of synthetic membranes (Matsuura *et al.*, 2008)

| Membrane type | Membrane structure | Preparation | Applications |
|--|--|--|--|
| Asymmetric cellulose, polyamide, polysulfone, polyacrylonitrile. | Homogeneous or microscopic skin on a microscopic substance | Casting and precipitation | Ultrafiltration and reverse osmosis, microfiltration, gas permeation, pervaporation. |
| Composite cellulose, polyamide, polysulfone | Homogeneous polymer film on a microporous substructure | Deposition on microporous substructure | Reverse osmosis, gas permeation, pervaporation |
| Homogeneous silicon rubber | Homogeneous polymer film | Extrusion | Gas permeation |

Table 2.3: (Continued)

| | | | |
|--|--|---|---|
| Ion exchanges divinylbenzene, polytetrafluoroethylene | Homogeneous or microporous copolymer film with positively or negatively charged fixed ions | Immersion of ion- exchanges powder in polymer or sulphonation and amination of homogeneous polymer film | Electrodialysis |
| Microporous : Ceramics, metal | 0.05-20µm pore diameter | Moulding and sintering | Gas permeation |
| Glass | 10-100µm pore diameter | Leaching from a two-component glass | Filtration (molecular mixtures) |
| Microporous: Sintered polymer polytetrafluoroethylene, polyethylene, polypropylene | 0.1-20µm pore diameter | Moulding and sintering | Filtration (suspensions, air filtration) |
| Microporous: Stretched polymer polytetrafluoroethylene, polyethylene | 0.1-5µm pore diameter | Stretching a partial crystalline film | Filtration (air, organic solvent) |
| Microporous: Track-etched polycarbonate, polyester | 0.02-20µm pore diameter | Irradiation and acid leaching | Filtration (suspensions, sterile filtration) |
| Symmetric microporous phase inversion cellulose | 0.1-10µm pore diameter | Casting and precipitation | Sterile filtration water purification, dialysis |

2.4 GAS SEPARATION BY USING MEMBRANE

Gas separation by selective permeation through polymer membranes is one of the fastest growing branches in membrane technology. Membrane gas separation has become one of the most significant new unit operations to emerge in the chemical industry in the last 25 years (Ismail *et al.*, 2002). Table 2.4 below shows application of membrane gas separation units.

Table 2.4: Gas membrane application (Nunes and Peinemann, 2006)

| Gas Separation | Application |
|----------------------------------|--|
| O ₂ /N ₂ | Nitrogen generation Oxygen enrichments |
| H ₂ /hydrocarbon | Refinery hydrogen recovery |
| H ₂ /CO | Syngas ration adjustment |
| H ₂ /N ₂ | Ammonia purge gas |
| CO ₂ /CH ₄ | Acid gas treating enhanced oil recovery landfill gas upgrading |
| H ₂ S/hydrocarbon | Sour gas treating |
| H ₂ O/hydrocarbon | Natural gas dehydration |
| H ₂ O/air | Air dehydration |
| Hydrocarbon/air | Pollution control hydrogen recovery |
| Hydrocarbon from process streams | Organic solvent recovery monomer recovery |

Organic polymer are the dominating materials for gas-separation membranes. But, Palladium alloys are the only inorganic materials that are currently used for gas separation which is ultrapure hydrogen generation on a commercial scale (Nunes and Peinemann, 2006). However, nowadays, inorganic materials have been developed with exciting unmatched selectivities for certain gas mixtures and some of inorganic membrane. Table 2.5 below shown relevant membrane material for gas separation.

Table 2.5: Materials for gas separating membranes (Nunes and Peinemann ,2006)

| Organic Polymer | Inorganic Polymer |
|-------------------------------|------------------------------------|
| Polysulfone, Polyethersulfone | Carbon molecular sieve |
| Celluloseacetate | Nonporous carbon |
| Polyimide, polyetherimide | Zeolite |
| Polycarbonate (brominated) | Ultramicroporous, amorphous silica |
| Polyphenyleneoxide | Palladium alloys |
| Polymethylpentene | Mixed conducting perovskites |
| Polydimethylsiloxone | |
| Polyvinyltrimethylsilane | |

Polymer membranes have been successfully used in many gas separation applications since polymeric membranes are permeable for all gases. Most of the important

membrane separation processes for current industrial interest or scientific work are mainly focused on glassy type polymers because of their superior gas selectivities and excellent thermal and mechanical properties (Ismail and Lorna, 2003). Nowadays, membrane glassy polymers are used for gas separation rather than rubbery polymers because of the high selectivity achieved. Glassy polymer is defined as an amorphous polymeric material that is below its softening or glass transition temperature, T_g while rubbery polymer is an amorphous polymeric material that is above its glass transition temperature, T_g under the conditions used (Stern, 1994). These materials offer enhanced mobility selectivity as compared to rubbery polymers due to the more restricted segmental motions in glassy polymers,. Since they are inherently more size and shape selective than rubbery materials, glassy polymers are more commonly used as the selective layer in gas separation membranes.

2.5 CHARACTERISTICS OF MEMBRANES FOR GAS SEPARATION

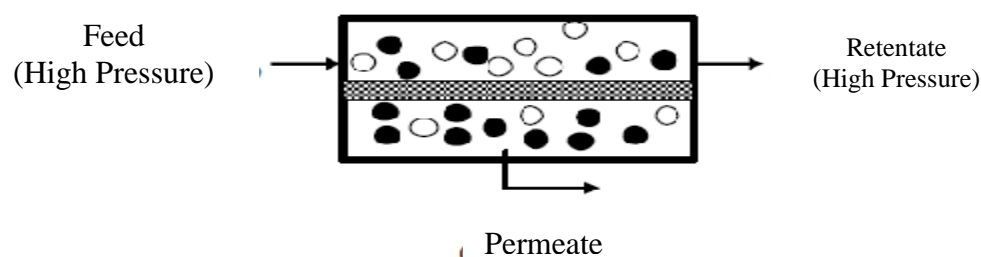
Comparing to other well-developed gas separation process, such as cryogenic distillation, pressure swing adsorption, and liquid absorption, membrane gas separation has the following features:

- a) Membrane gas separation does not involve phase change
- b) Membrane gas separation is efficient for bulk separation. The driving force for gas permeation is the partial pressure differences across the membrane. Generally, it is no significantly economical to obtain products with very high purities due to the quite low driving force available under this condition (Peinemann and Pinnau, 1988)
- c) The membranes are modular in design and easy to scale up. They can be used in either a large or small processing capacity without economy of scale. At small to medium scales, membrane is generally more competitive than the traditional separation technologies.
- d) Membrane can be easily integrated with other separation techniques so that the hybrid processes will be more effective than by using either technique alone.

- e) Membrane gas separation is environmentally friendly. It does not require additional mass agent for separation and thus does not generate secondary waste (e.g. vapor, solvent and solid particles).
- f) Membranes are compact and light, easy to operate and maintain (Pandey and Chauhan,2001)

2.6 FUNDAMENTAL OF GAS PERMEATION

Figure 2.1 below shows the typical membrane process for gas separation process essentially involves contacting one side of a semi-permeable gas separation membrane with a feed gas mixture containing at least the gas whose enrichment is desired, along with one or more gases. The stream to be separated is fed to the membrane device at an elevated pressure, where it passes across one side of a membrane. The opposite side of the membrane is held at a lower pressure. The pressure difference across the membrane provides the driving force for the diffusion of gas across the membrane. Separation is achieved because of differences in the relative transport rates of the feed components. Components that diffuse more rapidly become enriched in the low-pressure permeate stream, while the slower components are concentrated in the retentate or residue stream. Separation is achieved only if the system is not maintained in a state of equilibrium. A membrane will separate gases only if some components pass through the membrane more rapidly than others.



Note

● Fast Permeate Gas
○ Slow Permeate gas

Figure 2.1: Typical membrane process for gas separation